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Cost-Effective Chemical Enhanced Oil Recovery

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Abstract: *The increase in supply of crude has led to a dramatic slump in its price which has refused to bounce back as initially speculated. In effect, oil and gas industry is experiencing turmoil in its businesses and operations; therefore it is essential that there is a re-structure in these activities to negate the effect. This can only be attained if it adopts a smarter and cost-effective approach. The only acceptable condition under which chemical enhanced oil recovery can continue to apply in this era of low crude oil price is if the chemicals are cheap, multifunctional and considered to be smart. This study presents a review of chemical enhanced oil recovery and its applicability in uneconomic times. The success of CEOR is highly dependent on the microscopic and macroscopic recovery mechanisms involved as well as the reservoir rock physico-geochemical nature. Synergistic methods in CEOR is considered to be cost-effective as they exploit a combination of recovery mechanisms simultaneous in order to improve sweep efficiency, however before deployment, the technique and design must be tested extensively via lab core floods, pilot projects and dedicated numeric simulations. A Cheaper and potentially cost-effective chemical agent is the new breeds of giant-molecule surfactants. A special type of polymeric surfactants is the wormlike micelle solutions that even have superior rheological properties as they possess the tendency to increase recovery at minimal cost.*

Keywords: *Chemical Enhanced Oil Recovery, Cost-effective, Synergistic CEOR, EOR, Polymeric Surfactants.*

1. Introduction

The recent drop in crude oil price as remained for over a year at around $50 to $60/barrel. This is a reflection of strong energy market forces which could be attributed partly to the recent boom in shale hydrocarbon exploration that led to continuous production and significant increase of crude oil in circulation. Lately, this period is being referred to as the age of ‘abundance’. In contrast to initial speculations, the market value of petroleum crude refuses to bounce back. Hence, it is being deliberated amongst producing countries, multinational operators and other stakeholders that the era of $100/barrel and beyond might be over and the oil and gas industry should brace itself for the new regime. Already, the ripple effect of the new price is being felt in the businesses and operations in the industry. Massive downsizing of workforce is taking place across all facets from the state-owned oil companies to the international operators and service providers. A lot of projects are abandoned because of the uncertainties that come with the reduced price which has led to losses in revenue.

The reality that the oil price slide might not be reversed because of continuous production by both OPEC and the US with one of the major motives being the said need for a paradigm shift in evaluation of crude is fully dawn on the oil and gas industry. Therefore, in order to survive the harsh times, the exploration, production and processing industry must restructure their business operations and reset their financial goals. Here, financial decisions must be based on stringent economic standards. So also, in their technical and business operations, there is an urgent need to develop smart and cost-effective systems - a learning system that aims to reduce cost and improve efficiency, a system that can do more with fewer resources which is multifunctional, Flexible and adaptable has it continues to evolve with the dynamics of economics of petroleum.

In times as this, the techniques and options for developing a new field or continuous operation of an old field are those that strive to reduce operational cost by all possible means while making attempt to increase recovery. Naturally in cases where there is a substantial decrease in the price of crude, enhanced oil recovery methods like chemical flooding are considered to be unattractive in every way, however, there’re operational strategies that can be employed for applying chemical enhanced oil recovery in a cost-effective manner. Thus, based on the fundamentals behind the various types of chemical flooding, this review aims to draw attention and reveal how the EOR technique can be utilized efficiently even in times of low crude price. The discussions will be limited to the technical aspect and the physics behind increase in recovery in chemical flooding, leaving out the economics.

2. Application of Chemical Enhanced Oil Recovery

To be justified as an option for developing matured reservoirs and brownfields in the era of low price crude oil, EOR methods using chemicals must be highly efficient and cost-effective. In other words, they must have high potency to recover substantial additional barrels which can't be attained using primary and secondary recovery schemes, and at minimal cost of deployment.

Periods of increase in crude oil price have always serve as times when EOR techniques are given consideration for exploiting depleted reservoirs, however, studies have revealed coupled with practical field experience that proper field development plans should give allowance for secondary, tertiary and hybrid injection schemes as they contribute to sweep efficiency (INTSOK, 2011; Bunger et al., 2013; Thakur, 1990). Recently, a lot of unconventional reservoirs are being produced and chemical EOR methods are one of the viable options considered for their development (Fortenberry, 2013; Bryan et al., 2008).

CEOR entails the injection of chemical agents to boost areal and vertical or lateral sweep by enhancing microscopic and macroscopic displacement mechanisms, as illustrated in equation (1) and (2). Here, theClasses of chemicals usually employed are polymers, surfactants, low salinity water and alkalines. Every CEOR scheme is designed to explore certain recovery mechanisms which are deduced after extensive laboratory studies and pilot projects before upscaling to field level. Tertiary recovery mechanisms using Chemical methods are reservoir-specific because the design must take into cognizance the salinity and PH environment as well as the reservoir rock geochemistry in order to record success.

$$E = E_v \times E_D \tag{1}$$

Where $E_V = E_L \times E_A$ (2)

E is overall hydrocarbon displacement efficiency

E_v is the macroscopic displacement efficiency

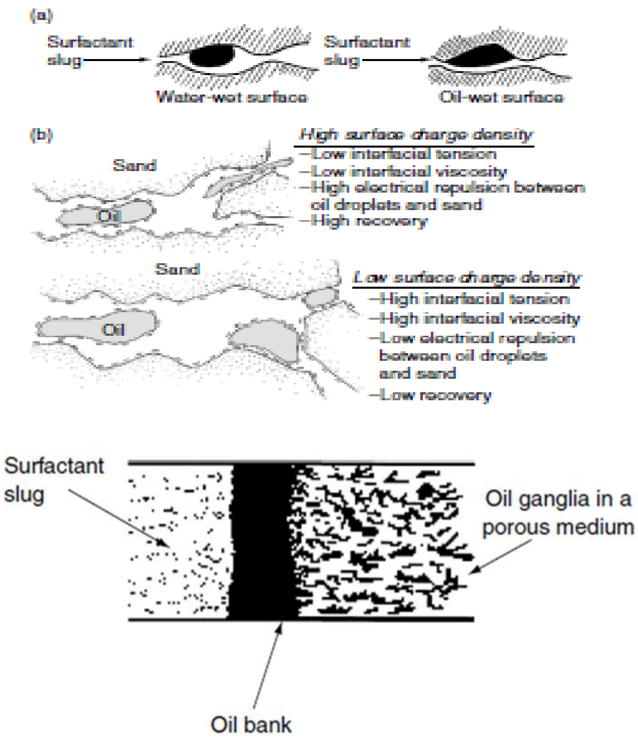
E_L is the lateral sweep efficiency

E_D is the microscopic displacement efficiency

E_A is a real sweep efficiency

3. CEOR Recovery Mechanisms

3.1. Interfacial Tension Lowering



(c)

Fig1. *Surfactant action in altering capillary forces in pore spaces for oil recovery*

Introduction of surface-active chemicals into pore spaces containing multiphase fluids will reduce the forces of adhesion at their interfaces leading to reduction of capillary pressure that exists therein. Most reservoir rocks are either water-wetting or mixed-wetting meaning at its lowest saturation, water lines the surface of grains within the pore spaces while the non-wetting phase exist as a globule at the centre. A high interfacial tension will translate to high capillary pressure which implies that fluids are withheld by the rock and they are having low relative permeability's. However, as the capillary pressure is reduced, there is mobilization and displacement of trapped fluids between inter connected pore networks. Surfactants are the commonest class of chemicals used for IFT lowering processes in EOR.

3.2. Wettability Alteration

It involves changing the surface characteristics of rock grains by its interaction with chemical agents either via physical adsorption or reaction with rock minerals. Imbibitions of the wetting phase unto rocks can lead to entrapment of less-wetting or non-wetting phase in multiphase reservoirs therefore, by altering the wettability properties, the trapped hydrocarbons are released by the boosting of their relative permeability's. This particular recovery mechanism has been proposed for low-permeability gas-liquid reservoirs where gas is experiencing choked-flow due to liquid drop out (Wu and Firoozabadi, 2010; Li et al., 2011). Surface active agents are best suited for this.

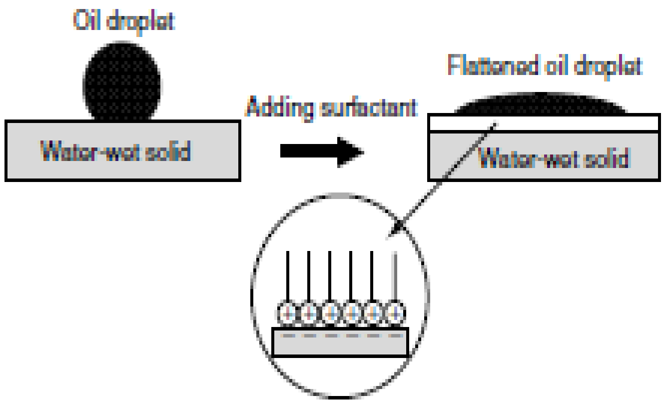


Fig2. *Wettability alteration by addition of surfactants*

IFT lowering and wettability alteration are ways by which the capillary forces can be manipulated to increase recovery while the saturation of the wetting phase in a reservoir is a major determinant, as depicted in figure 3.

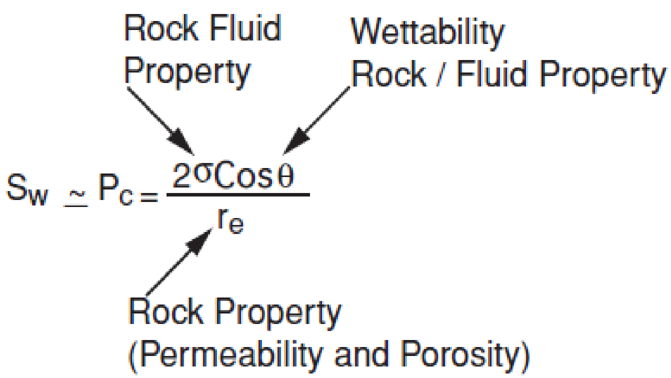


Fig3. *Relationship between capillary forces, rock and fluid properties*

3.3. Mobility Control

Increasing viscous forces in porous media by thickening the aqueous or the displacing phase in contrast to the oleic or the displaced phase enhances the displacement process. Here, displacement is stable and its efficiency is enhanced as mobility ratio is reduced as shown in equation (3). In CEOR, increasing the resistance to flow of the displacing phase by agents like polymers prevents 'viscous fingering' which could lead to poor sweep of the targeted reservoir section. This is the principle behind polymer-augmented water flooding.

$$M = \frac{\lambda_w}{\lambda_o} = \frac{k_{rw}/\mu_w}{k_{ro}/\mu_o} = \frac{k_{rw}\mu_o}{k_{ro}\mu_w} \quad (3)$$

The overriding of the displaced phase by the displacing phase eventually develops into phase trapping. While this is a major challenge in secondary recovery schemes like water flooding, chemical flooding can be used to prevent this phenomenon by adjusting the capillary and viscous forces that resides in the porous media so that displacement process will be favoured. This can be attained by either increasing the viscosity alone or reducing the capillary pressure simultaneously as demonstrated in the application of multiple CEOR agent at a time. The process has proven to be effective in increasing recovery and reducing residual oil saturation when a dimensionless ratio called capillary number is increased.

$$N_c = \frac{v\mu}{\sigma \cos\theta} \quad (4)$$

Where $\sigma \cos\theta$ is a representation of the capillary force in a pore spaces

$v\mu$ is representation of viscous force

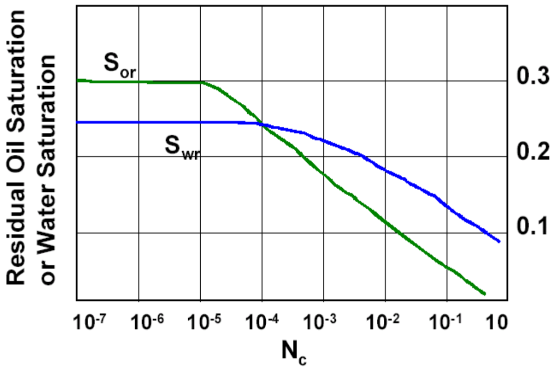


Fig4. *Typical capillary desaturation curve*

3.4. Permeability Reduction

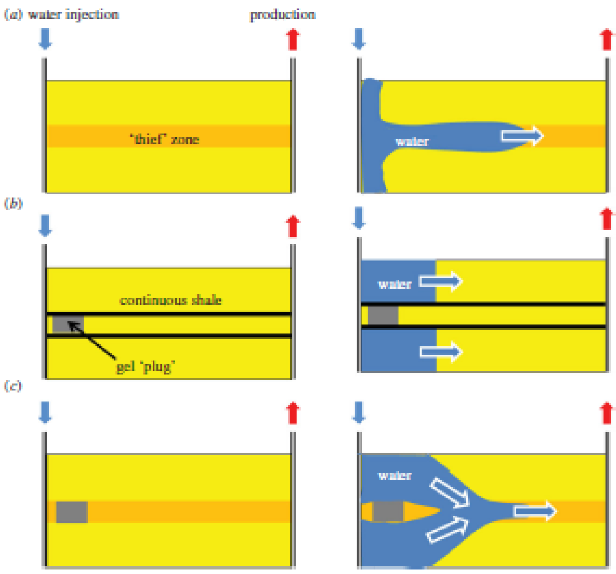


Fig5. *Selective permeability reduction*

The challenges of producing a highly heterogeneous reservoir by secondary recovery techniques can be overcome using Chemicals. These reservoirs are characterized by interplay of high permeable streaks with tight spots. The 'thief zones' serve as channels for injected drives while bypassing hydrocarbons in the tight spots resulting into an ineffective sweep of the reservoir. However, with the

Injection of cross-linking agents which selectively reduces/plug high permeability streaks, the secondary drives are re-channelled to the oil-bearing zones and we can have a proper sweep. The process can be designed in a way that the agents are cross-linked before injection or the cross-linking is activated in-situ using the right catalyst (Kim, 1995). The recovery mechanism can be regarded as a standalone chemical enhanced recovery process or just a technique to boost secondary recovery schemes. Polymers gels are the commonest agents for this method.

4. SYNERGISTIC METHODS IN CEOR

The main aim of tertiary recovery techniques is to engage either one of the microscopic forces that are present in the porous media or the three simultaneously to improve recovery using external energy sources, the forces being capillary force, viscous force and gravitational forces. This is an attempt to improve the efficiency and ultimately the cost-effectiveness of enhanced recovery programmes. While chemical enhance oil recovery concentrates majorly on the manipulation of the first two types of forces, it involves a Sequential or simultaneous injection of different classes of chemicals to perform specific functions so as to exploit the available recovery mechanisms. Common Examples of synergistic methods are surfactant-polymer flooding, alkaline-surfactant-polymer flooding and micellar-polymer flooding.

Generally, Multi-component chemical flooding design involves an initial injection of a preflush; this is to condition the reservoir salinity and PH, as well as the geochemical state so that it will be suitable for the main EOR agent.The main slug is injected afterwards to exploit the targeted recovery mechanism for mobilization. The mobilized hydrocarbon is then displaced with a buffer solution. This particular solution has the capacity to systematically sweep the reservoir of de-trapped hydrocarbons in order to improve the efficiency of the process; hence, they are crucial to the success of EOR programmes. The concentration of the buffer solution in the aqueous phase is reduced gradually as all the injected components are flushed and driven towards the production wells.

While micellar-polymer used to be the commonest for light and medium crudes (Lowry et al., 1986), alkaline-surfactant-polymer has recently received a lot of attention even for heavy oils (Speight, 2009). Improved Recovery factors with incremental costs as low as $2.42/incremental barrel can be achieved (Stoll et al., 2011). The alkaline performs the function of conditioning the reservoir against excessive adsorption of surfactant and polymer by maintaining a low salinity and high PH by reacting with the acidic content of crude to form soap in-situ which aids in reducing interfacial tension. Though, according to study (Fortenberry, 2013), alkali-acidic crude reaction increases the hydrophobicity of the aqueous system, introduction of surfactants help to balance the chemical condition in porous system during displacement.

Application of chemical flooding was showing a lot of promises between the late 1970s to mid-eighties before the price slump (Alvarado and Manrique, 2010). Lately, with the number of matured fields and unconventional reservoirs on the increase, CEOR is coming on-stream again with largest volume being ASP application in China (Chang et al, 2006; Demin et al, 1999; Qu et al. 1998) and Oman(Stoll et al., 2011). MP, SP and AP too have been widely applied in other countries like USA, Indonesia, Canada and India (Bou-Mikael et al., 2000).

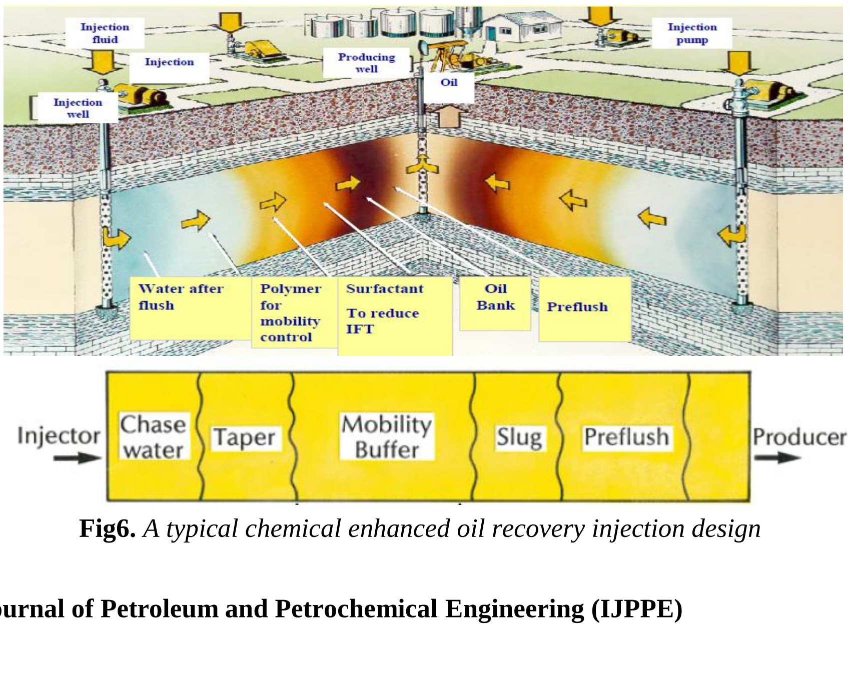


Fig6. *A typical chemical enhanced oil recovery injection design*

Synergistic chemical flooding entails extensive laboratory investigations, pilot tests field and numerical simulation of core floods and the full field before the reservoir application can be implemented. Most experiments aim to determine optimum salinity and PH for microemulsion-induced low IFT conditions in porous media. Samanta et al. (2012), carried out a study to investigate the effect of different concentration of components on ASP flooding performance (see table 1) and coupled with a detailed cost analysis, was able to determine an optimum system composition. Another studydemonstrated how alkaline-surfactant can be used to improve heavy oil recovery while highlighting the dominant recovery mechanisms using microemulsions (Bryan et al., 2008). Highly sophisticated chemical flooding simulators have been used to design and evaluate the performance of ASP and SP for both corefloods (Douarche et al., 2013) and full field injections (Anderson, 2006; Sarkar, 2012).

Table1. *Comparison of alkaline-surfactant-polymer with surfactant, polymer, alkaline floods.*

Expt. No.	Porosity (%)	Permeability, k (darcy)		Design of chemical slug for flooding	Recovery of oil by water flooding at 95 % water cut (% OOIP)	Additional recovery (% OOIP)	Saturation (%)		
		k_w ($S_w = 1$)	k_o (S_{wi})				S_{wi}	S_{oi}	S_{or}
S1	38.665			0.5 PV NaOH (0.5 %) + chase water	50.71	13.88	19.1	80.9	25.4
S2	37.265	1.235	0.218	0.5 PV 1,500 ppm PHPAM + chase water	52.65	16.12	18.51	81.49	22.96
S3	38.665	1.234	0.212	0.5 PV SDS (0.1 %) + chase water	51.65	17.96	19.09	80.91	20.2
S4	36. 805	1.224	0.213	0.3 PV 0.1 % SDS + 0.2 PV 2,000 ppm PHPAM + chase water	51.35	20.99	15.00	85.00	22.87
S5	37.265	1.144	0.217	0.3 PV (0.5 % NaOH + 0.1 % SDS + 1,500 ppm PHPAM) + 0.2 PV 1,500 ppm buffer + chase water	50.20	23.69	18.52	81.48	20.49

There has been lately a growing interest in developing new combination recovery mechanisms for chemical enhanced oil recovery. While most efforts have been directed towards generating and activating recovery agents in order to introduce new or hybrid recovery mechanisms in-situ after injection, others are working to better already existing synergistic methods. A good example is surfactants that are only activated upon contact with reservoir hydrocarbons (Romero-zeron, 2012). A new CEOR method was invented and coined as ACP(Alkaline Co-solvent-Polymer) flooding at the university of Texas, Austin to exploit heavy hydrocarbons(Fortenberry, 2013).The particular method is supposed to be an improvement on the shortcomings of ASP and AP methods. Another technique, adopted from soil remediation processes, is the SEPR (surfactant enhanced product removal). It makes use of a blend of surfactant/co-solvent and peroxide systems. Here, the peroxide reacts with minerals and organic component of the rock to generate oxygen which combines with the surfactant blend to release oil from capillary spaces via combination of mechanisms like viscosity reduction of hydrocarbon, IFT lowering, solubilisation and emulsification (Hoag and McAvoy, 2012). Efforts are being made to optimize the process for Minnelusa reservoir in Wyoming.

The argument for synergistic techniques in exploiting depleting reservoirs is tangible from the cost-effective and operational efficiency point of view. However, this doesn't eliminate the fact that multicomponent chemical injection is an expensive process (Bunger, 2013; Alvarado and Manrique, 2010; Romero-zeron, 2012). Apart from the development and testing stage at laboratory and pilot scale, the cost of manufacturing and procuring series of chemicals for field application can't be overlooked. Also, Storage and mixing in production facilities will pose challenges that won't come without their respective costs. It will suffice to say that deployment in offshore facilities will further magnify the cost and risk attached.

Looking at the technicality of multicomponent CEOR projects, their performances tend to be lower than expectation frequently because of some logical reasons. The proposed mechanism of recovery would have been proven during the testing stage but ends up failing for field application which is partially attributed to poor injection design. Also, there is Susceptibility to chemical and mechanical degradation in-situ because of unfavourable physico-geochemical conditions (Muggeridge et al., 2015). In a highly heterogeneous reservoir with tortuous pore network, Chromatographic separation of multicomponent chemical system tends to develop which will be detrimental to the success of the process design (Nuiyabin, 2001). Also, chemical agents experience retention due to adsorption or mechanical trapping at pore throats.

These two sets of factors point to the need to develop cheaper, more cost-effective chemicals that have high tolerance to harsh reservoir conditions and that are more adaptable to physical geometry of the porous media. The following discussion below aims to provide a solution to these challenges.

5. POLYMERIC SURFACTANTS

These are new breeds of chemicals that are being studied for EOR programmes (Pope, 2011). They're long chain polymer-like surfactantswith potentials to improve recovery using a combination of microscopic recovery mechanisms simultaneously by the virtue of their molecular structure (Wang et al., 2014). They can be referred to asSmart chemicals because of their multifunctionality and the potential to beCost-effective.Being a single component chemical EOR agent, their use will be quite inexpensive unlike the common ternary and quaternary systems used for synergistic recovery methods which is prone to failure due to reasons discussed earlier.

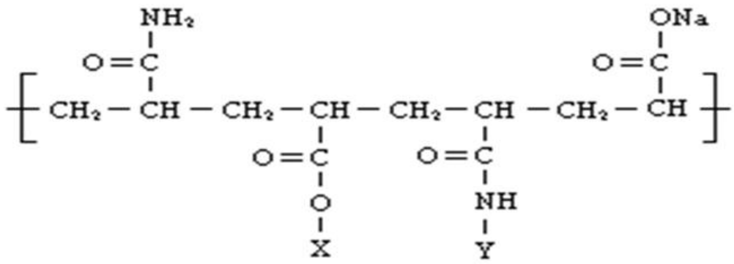


Fig7. *Molecular unit of a sample Polymer surfactant (Wang et al, 2014)*

A unique class of these chemicals is the Viscoelastic Surfactants**.**They are not polymers per se because the long chains are formed by aggregation and entanglement. When surfactants concentration gets to a certain level in a solution, which is critical micelle concentration, the molecules assemble and form aggregates known as micelles in solution. These micelles can take different morphological forms depending on the concentration and molecular characteristics of the surfactant. TheWorm-like micelles are formed at CMC of surfactants in the presence of salts (Kanicky et al., 2001; Kefi et al., 2005; Kumar et al., 2014). They are essentially surface-active and because of their chemistry and morphological structure, they are highly viscous, giving them the capacity to increase the viscosity of their residing aqueous system at low concentrations. They exhibit linear viscoelasticity, hence Maxwell fluids. During propagation, the worm like strains can deform and reform in order to relieve the aggregate of stress and by so doing the chemical exhibit a reversible rheological property which imparts elasticity.

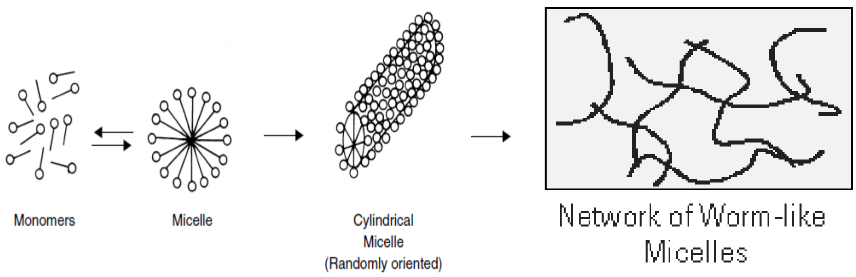


Fig8. *Transformation of surfactant monomers into entangled strains*

Table2. *Surfactants and corresponding salts (Kumar et al., 2014)*

Surfactant	Salt/Co-surfactant	References
Hexadecyltrimethylammonium bromide	Sodium nitrate, sodium chloride or sodium bromide	Kuperkar *et al.* (2008)
Sodium oleate	Octadecyldecyltrimethylammonium bromide	Ziserman *et al.* (2009)
Sodium dodecyl sulfate or sodium dodecyl trioxyethylene sulfate	Sodium oleate	Ishizuka *et al.* (2009)
Polyoxyethylene dodecyl ether	Polyoxyethylene cholestryle ether	Acharya and Kunieda (2003)
Sodium dodecyl sulfate	Tetradecyl dimethylammonium propane sulphonates+sodium chloride	Lopez-Diaz and Castillo (2010)

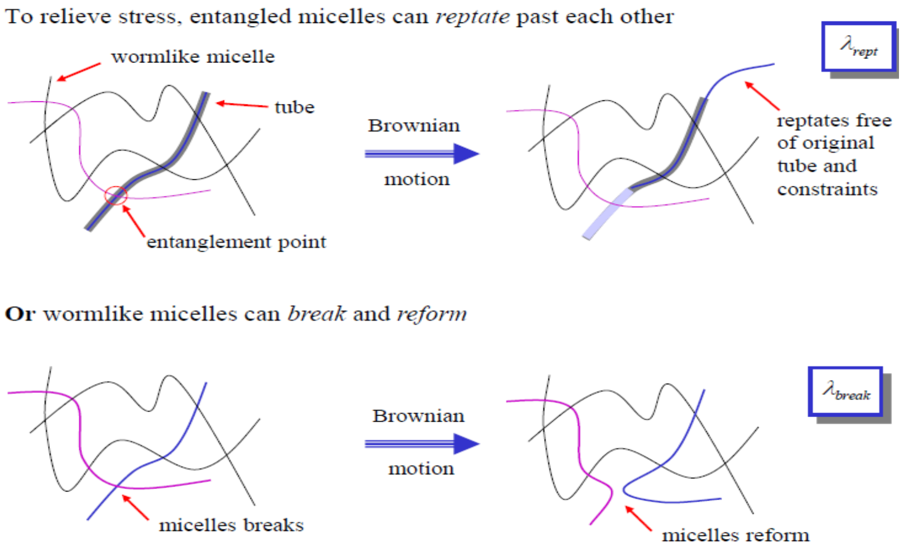


Fig9. *Stability of viscoelastic surfactants*

The viscoelastic surfactants can exhibit all the properties of polymer surfactants as well as that of normal polymers. However, the VES has additional properties that make them better candidate for CEOR as compared to the former two. Besides the fact that they can increase aqueous phase viscosity significantly at low concentrations, Strain hardening property under extensional flow conditions make them good candidates for mobility control processes while reversible shear thinning and thickening under high shear rates gives them good transport and displacement properties while propagating through heterogeneous, tortuous and tight reservoirs. Also, it has been reported that the viscoelastic surfactants are quite stable in conditions of high salinity and elevated temperature (Oil Chem Technologies, 2014). The synergistic recovery mechanism would come from the mobility control and interfacial tension lowering abilities with the potential to alter the wettability of the rock not to mention options for salinity self-conditioning using different salt solutions for worm-like micelles generation process.

Table3. *A comparison between polymers and viscoelastic surfactants (Oil Chem Tech)*

POLYMER	HIGH TEMP	HIGH TDS	HIGH SHEAR	COST
Polyacrylamide	75°C	poor	poor	low
AMPS copolymer	90°C	fair	poor	medium
Xanthan gum	50°C	fair	fair	high
Scleroglucan	100°C	fair	fair	high
Viscoelastic surf.	150°C	excellent	excellent	low

Viscoelastic surfactants have seen wide use on oilfields mostly as additives for drilling and completion fluids, especially fracturing jobs. This is mainly due to the fact that they have superior rheological properties and they don't leave residues which eventually clog channels unlike conventional polymers. Although their potentials have not been exploited as chemical EOR agents, studies have been carried out via core flooding experiments to investigate their supplementary capability to conventional polymers (Zhu et al., 2013; Yao et al., 2013), and their performances have been encouraging so far. While it's established that micelles can attain ultra–low interfacial tension in capillary spaces, rod-likes are very unstable in the presence of hydrocarbons leading to loss of viscosity and elasticity. Also, there're a lot of uncertainties as to the rate at which wormlike morphological structure and entanglement can be re-established after passage through tight constrictions as that of low permeability reservoirs (Rothstein, 2008). Hence, the success of their application as single component injection agents for chemical enhanced oil recovery is Benton extended works to improve and overcome these shortcomings.

6. Conclusion

From the discussions, an attempt has been made towards establishing that chemical flooding as an EOR technique can be used for producing depleting assets/matured reservoirs in the era of low price oil if the EOR agent is cheap, and it's considered to be a smart fluid with capacity for multi functionality. In-light of this, Polymeric surfactants can be regarded as very good example of a smart chemical EOR agent.

In order to boost the prospects and applicability of CEOR, The research industry should concentrate more on how to further improve the functionality of smart chemicals. This can be done by Designing EOR agents that will incorporate either new or more recovery mechanisms that can be implemented in-situ. Also, developing high-tolerance chemical agents will prevent degradation and sustain recovery in the presence of reservoir fluids.

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